

to a body derived from 3 atoms of this aldehyde, in which 2 (O₂) is replaced by 2 (I₂).

3 atoms of oil of bitter almonds, Oxyiodide of Benzaldehyde,
 $C_{42}H_{18}O_6$ $C_{42}H_{18}O_2I_4$.

In the case of acrolein, the action of hydrochloric acid is different ; it combines directly with it, no elimination of water taking place. If we conceive, however, that, in the action of this acid on common aldehyde, the water which is there produced is the effect of a further decomposition, then we may readily suppose that, if this further decomposition had taken place in the case of hydrochloric acid and acrolein, a body derived from two atoms of acrolein, and having O₂ replaced by Cl₂, corresponding to the second term in the combination of aldehyde and chlorine, would have been the result ; thus—

2 atoms of hydrochlorate of acrolein—

$C_{12}H_{10}O_4Cl_2 - 2(HO) = C_{12}H_8O_2Cl_2$, corresponding to the
 term $C_9H_8O_2Cl_2$ in common aldehyde.

There is a curious connexion which may be mentioned, in this substitution of chlorine for oxygen in aldehyde, between the formula of these bodies containing chlorine, and those of the isomeric modifications of aldehyde.

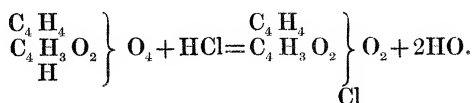
V. "On the Action of Acids on Glycol" (Second Notice.) By
 Dr. MAXWELL SIMPSON. Communicated by Dr. FRANK-
 LAND. Received June 29, 1859.

Since my last communication to the Society, I have discovered a more convenient process for the preparation of chloracetine of glycol. I have ascertained that the monoacetate of glycol is as readily converted into this substance by the action of hydrochloric acid, as a mixture of acetic acid and glycol. As the monoacetate is easily obtained, and for this purpose need not be quite pure, it is possible by this method to prepare the body in question on a large scale and with great facility. It is simply necessary to conduct a stream of dry hydrochloric acid gas into the monoacetate, maintained at the temperature of 100° C., till the quantity of oil precipitated on the

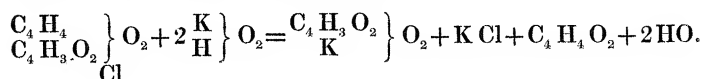
addition of water ceases to increase. The whole is then well washed with water, dried by means of chloride of calcium, and distilled. Almost the entire quantity passes over between 144° and 146° C. A portion of liquid prepared in this manner gave the following numbers on analysis, which leave no doubt as to its identity :—

	Theory.	Experiment.
C ₈ . . .	39·18	39·01
H ₇ . . .	5·71	5·83
O ₄ . . .	26·14	..
Cl . . .	28·97	..
	<hr/> 100·00	

The reaction which gives birth to this body may be thus explained :—



I have made a determination of the vapour-density of chloracetine, and obtained results confirmatory of the formula I have given for this body : experimental vapour-density 4·369, calculated 4·231 for 4 volumes. I have also ascertained that oxide of ethylene is formed, and not glycol, when this substance is acted upon by a solution of potash. The following equation will explain the reaction :—



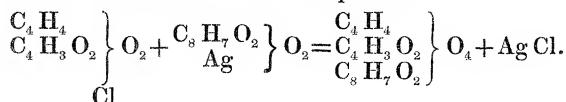
Action of Chloracetine of Glycol on Butyrate of Silver.—Formation of Butyroacetate of Glycol.

Equivalent quantities of chloracetine and butyrate of silver were exposed in a balloon with a long neck to a temperature ranging between 100° and 200° C., till all the silver salt had been converted into chloride. The product was then digested with ether, filtered, and the filtered liquor submitted to distillation. As soon as all the ether had been driven off, the thermometer rose rapidly to 180°, and between that temperature and 215° almost the entire quantity passed over. This was fractioned, and the portion distilling between 208°

and 215° was set apart for analysis. The numbers obtained lead to the formula $\left. \begin{matrix} \text{C}_4\text{H}_4 \\ \text{C}_4\text{H}_3\text{O}_2 \\ \text{C}_8\text{H}_7\text{O}_2 \end{matrix} \right\} \text{O}_4$, as will be seen from the following percentage table:—

Theory.	Experiment.	
	I.	II.
C ₁₆ 55·17	54·31	55·58
H ₁₄ 8·04	8·20	7·97
O ₈ 36·79
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100·00		

I also made a determination of the acids by heating a weighed quantity of the ether with hydrate of baryta in the usual manner. The quantity of sulphate of baryta obtained indicated 2·2 equivalents of acid for one equivalent of the substance analysed. The excess of acid was probably owing to the presence in the ether of a trace of free butyric acid. The following equation will explain the reaction which causes the formation of this compound:—



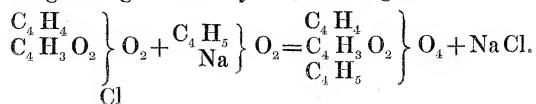
In many reactions chlorine replaces, and is replaced by, H + O₂; in this it is replaced by the group C₈H₇O₂ (equivalent to one atom of hydrogen) + O₂.

This ether, which I may call butyroacetate of glycol, has a bitter pungent taste. It is insoluble in water, but soluble in alcohol. It is specifically heavier than water. It is a very stable body,—solution of potash, even when boiling, effecting its decomposition with difficulty.

I have no doubt that many analogous compounds may be prepared in the manner I have just described.

Action of Chloracetine of Glycol on Ethylate of Soda.

In the hope of forming a compound intermediate between diacetate of glycol and diethylglycol, I resolved to try the action of chloracetine on ethylate of soda, thinking that probably the body in question might be generated by the following reaction:—



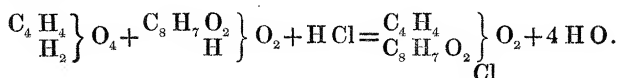
In order to settle this point, I exposed equivalent quantities of these bodies in a sealed balloon to the temperature of a water-bath for about two hours. My expectations, however, were not realized. On opening the balloon, I found that the reaction had proceeded too far, acetic ether having been formed along with the chloride of sodium.

Action of Hydrochloric and Butyric Acids on Glycol.—Formation of Chlorbutyrine of Glycol.

This compound is prepared in the same manner as its homologue, namely by transmitting a stream of dry hydrochloric acid gas through a mixture of equivalent quantities of butyric acid and glycol, maintained at the temperature of 100°C . As soon as the reaction is finished, the product is well washed with water, dried by means of chloride of calcium, and distilled. The greater part passes over between 160° and 182° . This must be rectified, and the quantity distilling between 175° and 182° collected apart. This gave, on analysis, results agreeing with the formula $\left. \begin{matrix} \text{C}_4\text{H}_4 \\ \text{C}_8\text{H}_7\text{O}_2 \end{matrix} \right\} \text{O}_2, \text{ as will be seen from the following table:—}$

	I.	II.
$\text{C}_{12} \dots 47.84$	47.76	..
$\text{H}_{11} \dots 7.30$	7.31	..
$\text{O}_4 \dots 21.28$
$\text{Cl} \dots 23.58$..	23.88

The reaction, to which the formation of this body is due, may be thus explained:—



Chlorbutyrine of glycol, as I may call this compound, has a pungent and somewhat bitter taste. It boils at about 190° . Its specific gravity at zero is 1.0854. It is insoluble in water, but freely soluble in alcohol. It is decomposed with difficulty by a boiling solution of potash, but readily by solid potash,—chloride of potassium, butyrate of potash, and oxide of ethylene, being formed.

I have ascertained that acetobutyrate of glycol, the ether I have

already described, can be prepared from this body as well as from chloracetine, by exposing it to the action of acetate of silver. The process is the same as that I have already given, with this difference, that the reacting bodies must not be heated above 150°C . The ether prepared in this manner gave the following numbers on analysis :—

	Theory.	Experiment.
C_{14}	55.17	56.29
H_{14}	8.04	8.75
O_8	36.79	..

The quantity of this substance at my disposal was so small (the greater part of my product having been lost) that I could not purify it completely ; hence the experimental numbers do not exactly accord with the theoretical.

Action of Hydrochloric and Benzoic Acids on Glycol.—Formation of Chlorbenzoate of Glycol.

A mixture of equivalent quantities of glycol and benzoic acid, previously fused and powdered, was exposed to the action of dry hydrochloric acid gas for several hours, the mixture being maintained at the temperature of 100° during the action of the acid, as in the case of the former compounds. The product thus formed presented the appearance of a soft white solid, and contained a considerable quantity of uncombined benzoic acid. This was removed by agitating it with hot water, till, on cooling, it no longer became solid, but remained perfectly fluid. Finally it was dissolved in alcohol, and precipitated by water. The body thus prepared, and without being distilled, was analysed, having been previously dried in vacuo over sulphuric acid. Another specimen, prepared in the same manner, at a different time, was also analysed, having, however, been previously distilled. During the distillation it was observed that not a drop of fluid passed over till the mercury had risen to 254° , and between that temperature and 270° the entire liquid distilled over. What passed over between 260° and 270° was collected separately ; this was the portion analysed. The numbers obtained on analysis

agree with the formula $\left. \begin{matrix} \text{C}_4 \text{H}_4 \\ \text{C}_{14} \text{H}_5 \text{O}_2 \end{matrix} \right\} \text{O}_2$, as the following table shows :—

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Theory.	Experiment.		Portion distilled.
	I.	II.	
C ₁₈ . . . 58·54	59·70	..	58·69
H ₉ . . . 4·87	5·01	..	5·31
O ₄ . . . 17·35
Cl . . . 19·24	..	17·93	..
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	100·00		

The portion not distilled contained doubtless a trace of free benzoic acid, which would affect the carbon and chlorine, but not the hydrogen.

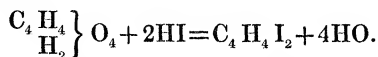
Chlor-benzoate of glycol, as I shall call this compound, has a pungent and somewhat bitter taste. It is insoluble in water, but freely soluble in alcohol and ether. Boiling solution of potash effects its decomposition with difficulty, solid potash readily, the reaction being the same as in the case of the analogous compounds.

Action of Hydriodic Acid on Glycol.—Formation of Iodide of Ethylene on Iodhydrine of Glycol.

Hydriodic acid gas is absorbed with great energy by glycol. A considerable quantity of heat is evolved during the passage of the gas, and the liquor becomes black and thick from the separation of free iodine. On removing the iodine by means of dilute potash, a mass of small white crystals is brought to light, which I at once suspected to be iodide of ethylene. To remove all doubt on this point, I submitted the crystals to analysis, having previously purified them, by recrystallizing from boiling alcohol. The numbers obtained agree with the formula of iodide of ethylene :—

	Theory.	Experiment.
C ₄ . . . 8·51	8·51	8·73
H ₄ . . . 1·42	1·42	1·78
I ₂ . . . 90·07	90·07	..
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	100·00	

The reaction which causes the formation of iodide of ethylene may be thus explained :—



That the action of hydriodic acid on glycol should be different

from that of hydrochloric acid is doubtless owing to the bond of union between hydrogen and iodine being much weaker than that between hydrogen and chlorine.

If, on the other hand, the temperature of the glycol be prevented from rising during the passage of the hydriodic acid gas, by surrounding the vessel containing it with cold water, a liquid product is obtained, which is coloured dark-brown by free iodine. This I have not as yet been able to discover any means of purifying, it being soluble in water, and decomposed by distillation. I believe, however, it is the compound corresponding to chlorhydrine of glycol $\left(\begin{smallmatrix} C_4H_4 \\ H \end{smallmatrix} \right) O_2$ discovered by M. Wurtz. A portion of this liquid,

Cl

from which I had simply removed the free iodine, by agitation with mercury, gave, on analysis, numbers agreeing tolerably well with the formula of iodhydrine. After the analysis, however, I discovered that it contained a considerable quantity of iodide of mercury in solution. Another portion, from which I had removed the iodine by means of metallic silver, gave, on analysis, 11.1 per cent. carbon and 3.5 hydrogen, instead of 13.9 carbon and 3.0 hydrogen. After all, an analysis is not necessary to enable us to arrive at the composition of this body. The products formed by the action of potash on it furnish us with almost as convincing a proof of its composition as any analysis could do. They are iodide of potassium and oxide of ethylene.

Iodhydrine of glycol is soluble in water and alcohol, but insoluble in ether. It has no taste at first; after a time, however, it almost burns the tongue, it is so pungent. It is decomposed by heat into iodide of ethylene, and probably glycol. It acts with great energy on the salts of silver.

Action of Hydriodic and Acetic Acids on Glycol.—Formation of Iodacetine of Glycol.

A stream of hydriodic acid gas was conducted into a mixture of equivalent quantities of glacial acetic acid and glycol, the temperature of which was prevented from rising during the action of the gas. As soon as a portion of the liquid gave a considerable quantity of an oily precipitate on the addition of water, the passage of the gas

was interrupted; for the prolonged action of the gas is apt to give rise to the formation of iodide of ethylene. The liquid thus obtained was well washed with very dilute potash, dried in vacuo, and analysed. The numbers obtained lead to the formula $\left. \begin{matrix} \text{C}_4\text{H}_4 \\ \text{C}_4\text{H}_3\text{O}_2 \end{matrix} \right\} \text{O}_2$, as will be seen from the following table:—

	Theory.	Experiment.	
		I.	II.
C ₈	22·42	21·95	22·30
H ₇	3·27	3·31	3·50
O ₄	14·96
I	59·35
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100·00			

Iodacetine has a sweetish pungent taste. It is insoluble in water, but soluble in alcohol and ether. Its specific gravity is greater than that of water. It crystallizes in tables when exposed to cold. Heated with potash, it gives iodide of potassium, acetate of potash, and oxide of ethylene. It is readily decomposed by the salts of silver.

This compound can also be prepared with great facility by exposing monoacetate of glycol to the action of hydriodic acid gas. The liquid must be kept cold during the action of the gas, which should be interrupted as soon as the addition of water to a portion of it causes an abundant oily precipitate. The whole is then washed with dilute potash, and dried in vacuo. A specimen prepared in this manner gave, on analysis, 22·62 per cent. carbon and 3·43 hydrogen, instead of 22·42 carbon and 3·27 hydrogen.

I hope soon to have an opportunity of studying these iodine compounds more particularly.

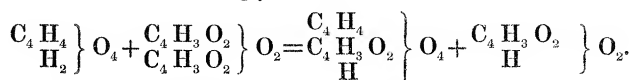
Action of Anhydrous Acetic Acid on Glycol.—Formation of Monoacetate of Glycol.

A mixture of equivalent quantities of anhydrous acetic acid and glycol was heated in a sealed tube for several hours at a temperature not exceeding 170° C. On opening the tube, and submitting its contents to distillation, it was observed that the mercury remained stationary for a considerable time at about 120°, the point of ebullition of glacial acetic acid, and then rose rapidly to 180°, between which and 186° the remainder of the liquid passed over.

This was analysed, and proved to be pure monoacetate of glycol.

Theory.	Experiment.
C ₈ 46·15	46·02
H ₈ 7·69	7·80
O ₆ 46·16	· . .
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100·00	

The following equation will explain the reaction which takes place between the acid and the glycol :—



The foregoing experiments were performed in the laboratory of M. Wurtz.

VI. "Experiments on some of the Various Circumstances influencing Cutaneous Absorption." By AUGUSTUS WALLER, M.D., F.R.S., Professor of Physiology, Queen's College, Birmingham. Received June 27, 1859.

In some former experiments* I endeavoured to elucidate the phenomena of cutaneous absorption on the lower animals (batracia), by immersing the hinder extremities in various solutions, and afterwards watching the period at which the absorbed substances reached the tongue, where their presence was detected by means of some reagent applied to its surface ; as, for instance, a salt of iron, when the legs were immersed in a solution of yellow ferro-cyanide of potassium ; Prussian blue was then formed as soon as the ferro-cyanide was brought to the tongue.

Furthermore, I was able to detect, by the aid of the microscope, the "lieux d'élection," or preference spots, where the cyanide escaped from the vessels.

On the present occasion I shall endeavour to elucidate cutaneous absorption on the higher animals, and, if possible, to give a more definite view of this function, by determining, by accurate measurement, the degree of rapidity, the peculiarities, &c., which it may offer in various conditions.

* Waller "Absorption of various substances through the skin of the Frog."—*Froiep's Tagesberichte*, 1851.